Spectroscopic fingerprints of a surface Mott-Hubbard insulator: the case of SiC(0001)

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We discuss the spectroscopic fingerprints that a surface Mott-Hubbard insulator should show at the intra-atomic level. The test case considered is that of the Si-terminated SiC(0001)$\sqrt{3}\times\sqrt{3}$ surface, which is known experimentally to be insulating. We argue that, due to the Mott-Hubbard phenomenon, spin unpaired electrons in the Si adatom dangling bonds are expected to give rise to a Si-2p core level spectrum with a characteristic three-peaked structure, as seen experimentally. This structure results from the joint effect of intra-atomic exchange, spatial anisotropy, and spin-orbit coupling. Auger intensities are also discussed.

Keywords: Semi-empirical models and model calculations; Photoemission; Auger electron spectroscopy; Magnetic phenomena; Surface electronic phenomena; Silicon carbide; Insulating surfaces.

The fractional adlayer structures on semiconductors show rich phase diagrams with potential instabilities of charge density wave (CDW) and spin density wave (SDW) type at low temperatures, as well as Mott insulating phases [1]. The (0001)$\sqrt{3}\times\sqrt{3}$ surface of hexagonal SiC, (as well as the closely analogous (111)$\sqrt{3}\times\sqrt{3}$ of cubic SiC) expected from standard LDA calculations to be a 2D metal with a half-filled narrow band of surface states in the bulk energy gap [2,3] – is instead experimentally proven to be an insulator with a rather large (2 eV) band gap [4,5]. It has been suggested that this system is a Mott insulator [6] due to the large value of ratio U/W, where U is the Coulomb interaction parameter, of the order of several eV, and W is the surface bandwidth, calculated to be about 0.35 eV [2,3]. Very recent STM data further confirm this picture [7].

A recent LSDA+U calculation [8] predicts an antiferromagnetic insulating state with 3×3 magnetic periodicity and a indirect gap of about 1.5eV, in reasonable agreement with the experimental value [4,5]. An exchange coupling J between neighboring Si adatoms of about $30K$ is also calculated. The LSDA+U magnetic state, with spin-collinearity enforced in the calculation, turns out to have a uniform magnetization $m^z = 1/3$: one spin-down and two spin-up adatom surface bands are completely filled in the 3×3 Brillouin zone. Crudely speaking, this corresponds to two adatom dangling-bond orbitals having spin-up electrons and one having spin-down electron in each triangular plaquette. When spin non-collinearity is allowed one finds, *e.g.,* from Hartree-Fock Hubbard model calculations, [8] that the state with spins lying on a plane – in a 120^o three-sublattice Néel structure, typical of the triangular lattice Heisenberg antiferromagnet [9] – has slightly better energy than the collinear one, but the resulting energy gain is so small, about 0.5 meV/adatom, that unrealistically precise ab-initio calculations would be necessary to decide which of the two is the actual ground state. Moreover, the bands for the two solutions are rather similar, apart from some extra splittings introduced by the collinear magnetic solution [8].

In reality, both the LSDA+U and the Hartree-Fock Hubbard calculations, being mean-field approaches are at best only cartoons for the actual Mott-Hubbard state, which is insulating not because it is magnetic, but rather due to strong correlations inhibiting electron hopping. Once this is appreciated, one realizes that – even in the absence of any true magnetic long-range order – finite magnetic moments on the Si adatoms should be experimentally detectable up to high temperatures, so long as there is an insulating gap. The low-temperature low-energy collective physics of these unpaired adatom spins is instead governed by a much smaller energy scale, the exchange coupling J. Is it conceivable that a genuine low-temperature spin long-range order (LRO) would be detectable in this quasi-2D system? It would seem unlikely, since: 1) The estimates for J already suggest that LRO, if present, must be there only at very low temperature. Moreover, thermal fluctuations might destroy LRO altogether, if the continuous spin symmetry is not broken by anisotropy effects due to spin-orbit coupling; 2) It is at present unclear which spin ordering will be stabilized by the spin-orbit coupling; 3) If spins lie on a plane, with zero net magnetization, they are presumably hard to detect with LRO sensitive techniques. Therefore, without ruling out totally the possibility of low-temperature LRO, we believe that the SiC(0001)$\sqrt{3}\times\sqrt{3}$ surface will most likely be in an overall paramagnetic Mott insulating state, in spite of the existence of an on-site moment, at least down to liquid nitrogen temperature.

It is the aim of the present paper to discuss in some detail what kind of experimental signatures one should look for in a surface Mott-Hubbard insulator, apart from a gap in the photoemission spectrum. As mentioned previously, methods which require magnetic LRO are likely not viable. The situation could be much more promising at the intra-atomic level. We will argue below that the very fact that the system is in a Mott-Hubbard insulating state, independently of the magnetic LRO issue, brings about unpaired spins in the adatom dangling bonds, which in turn determine exchange splittings in the adatom core levels which should be large and detectable. These splittings may

in fact have been already observed for SiC(0001) in the surface component of the Si-2p core level photoemission spectrum, [10] although attributed so far to some unspecified charge inequivalence of two types of Si adatoms.

To make things more concrete, let us assume that, due to the Mott-Hubbard phenomenon, the $3p_z$-like dangling bond orbital of the Si adatom in the $\sqrt{3} \times \sqrt{3}$ SiC(0001) is singly occupied by an unpaired electron, say of spin up. In reality, the Wannier function for the surface state is not a pure $3p_z$, since it extends itself down into the first SiC bilayer [2,8]: the weight α of the Si $3p_z$ orbital in the Wannier function is about 0.5, the remaining lobe having a negligeable overlap with the Si-adatom core [2,8]. The $3s$ and $3p_{x,y}$ orbitals of the Si-adatom are involved in the bonding with first-layer C atoms, and contain spin-paired electrons. Therefore, a Si-adatom has two distinct sources of anisotropy: i) the first comes about because the occupation α of the $3p_z$ orbital is not equal to the occupation, call it β, of the $3p_x$ or $3p_y$ orbitals; ii) the second, and most important, source of anisotropy is due to the fact that the electron in the $3p_z$ dangling bond is *spin unpaired*, as opposed to the standard singlet bonding configuration in $3p_{x,y}$. These anisotropies break the core level symmetry between $2p_z$ and $2p_{x,y}$ by an amount which we will argue to be not negligeable compared to spin-orbit. We will now estimate the expected $2p$ core level splittings, with and without a spin-orbit coupling, and show that while spatial anisotropy of type i) by itself would result in a very small effect, the spin induced anisotropy ii) has a large influence on the spectrum.

The calculation we perform is very simple, and is based on the Si $2p-3p$ Slater exchange and Coulomb integrals, obtained from pure atomic Hartree-Fock calculations. Assume the Si adatom valence electrons to be distributed with weights α in $3p_z\uparrow$, and $\beta/2$ in each $3p_{x,y}\uparrow$ and $\downarrow$. Let us consider first the situation in absence of spin-orbit coupling, $\lambda_{\rm SO}=0$. The Hartree-Fock energy of the $2p_z\uparrow$ states can be written as

$$\epsilon_{2p_z\uparrow} = \alpha[K_{2p_z,3p_z} - J_{2p_z,3p_z}] + 2\frac{\beta}{2}[2K_{2p_z,3p_x} - J_{2p_z,3p_x}] + \dots \ , \tag{1}$$

where the dots stand for one-body terms and two-body contributions due to other spin-paired occupied orbitals which will exactly cancel out in all the energy differences which we will calculate. Here $K_{2p_z,3p_{z(x)}} = \big(2p_z, 3p_{z(x)}|e^2/|\mathbf{r}_1-\mathbf{r}_2||2p_z, 3p_{z(x)}\big)$, and $J_{2p_z,3p_{z(x)}} = \big(2p_z, 3p_{z(x)}|e^2/|\mathbf{r}_1-\mathbf{r}_2||3p_{z(x)}, 2p_z\big)$, are the relevant $2p-3p$ Coulomb and exchange Slater integrals. The factor 2 in front of the $\beta/2$ term is due to equal contributions coming from $3p_y$ and $3p_x$. The factor 2 in front of $K_{2p_z,3p_x}$ keeps into account the direct contribution due to both $\uparrow$ and $\downarrow$ $3p_{x,y}$ electrons. (The corresponding exchange term has no factor 2 because only $3p_{x,y}\uparrow$ electron contribute to the exchange gain of the $2p_z\uparrow$ level.) A similar calculation for $\epsilon_{2p_x\uparrow} = \epsilon_{2p_y\uparrow}$ gives

$$\epsilon_{2p_x\uparrow} = \alpha[K_{2p_x,3p_z} - J_{2p_x,3p_z}] + \frac{\beta}{2}[2K_{2p_x,3p_x} - J_{2p_x,3p_x}] + \frac{\beta}{2}[2K_{2p_x,3p_y} - J_{2p_x,3p_y}] + \dots \ , \tag{2}$$

which can be reexpressed, due to rotational symmetry, in terms of the previously introduced $K_{2p_z,3p_{z(x)}}$ and $J_{2p_z,3p_{z(x)}}$. We now estimate the Slater integrals assuming pure atomic hydrogen-like $2p-3p$ orbitals (the effect of intra-atomic hybridization in a full atomic HF calculation would change a bit the numbers: these effects will be estimated later on). Numerically, the two different Coulomb integrals appearing in Eqs. 1-2 are large and comparable ($K_{2p_z,3p_z} \approx 30.5$ eV, $K_{2p_z,3p_x} \approx 28.2$ eV), whereas the $2p_z-3p_z$ exchange integral is smaller ($J_{2p_z,3p_z} \approx 4.3$ eV), but one order of magnitude larger than the $2p_z-3p_x$ exchange integral ($J_{2p_z,3p_x} \approx 0.5$ eV). The large difference between $J_{2p_z,3p_z}$ and $J_{2p_z,3p_x}$ immediately implies that the exchange splitting between $2p_z\uparrow$ and $2p_z\downarrow$ is rather large

$$\epsilon_{2p_z\downarrow} - \epsilon_{2p_z\uparrow} \approx \alpha J_{2p_z,3p_z} \approx 2eV$$

whereas the correponding exchange splitting between $2p_{x/y}\uparrow$ and $2p_{x/y}\downarrow$ is one order of magnitude smaller:

$$\epsilon_{2p_{x/y}\downarrow} - \epsilon_{2p_{x/y}\uparrow} \approx \alpha J_{2p_z,3p_x} \approx 0.2eV$$

We can also calculate, using Eqs. 1-2, the splitting $\Delta = \epsilon_{2p_{x/y}\uparrow} - \epsilon_{2p_z\uparrow}$ between the $2p_z\uparrow$ and the $2p_{x/y}\uparrow$ levels,

$$\Delta = \alpha[(J_{2p_z,3p_z} - J_{2p_z,3p_x}) - (K_{2p_z,3p_z} - K_{2p_z,3p_x})] + \frac{\beta}{2}[2(K_{2p_z,3p_z} - K_{2p_z,3p_x}) - (J_{2p_z,3p_z} - J_{2p_z,3p_x})] \ . \tag{3}$$

Notice that the structure of the α contribution in Eq. 3 differs from that of the β term because the $3p_z$ is assumed to be spin unpaired (anisotropy ii), above): If we were to assume that the occupancy α was due $\alpha/2$ $3p_z\uparrow$ and $\alpha/2$ $3p_z\downarrow$, the α term would be given by $(\alpha/2)[(J_{2p_z,3p_z} - J_{2p_z,3p_x}) - 2(K_{2p_z,3p_z} - K_{2p_z,3p_x})]$ and would exactly cancel off the β term when $\alpha=\beta$ (bulk case). Plugging in the numbers for the Coulomb and exchange integrals we get $[2(K_{2p_z,3p_z} - K_{2p_z,3p_x}) - (J_{2p_z,3p_z} - J_{2p_z,3p_x})] \approx [2(2.3eV) - 3.8eV] = 0.6eV$, and $[(J_{2p_z,3p_z} - J_{2p_z,3p_x}) - (K_{2p_z,3p_z} - K_{2p_z,3p_x})] \approx [3.8eV - 2.3eV] = 1.5eV$, which provide the desidered estimate for $\Delta \approx \alpha[1.5eV] + (\beta/2)[0.6eV]$, i.e.,

$\Delta \approx 1eV$ for $\alpha \approx 0.5$ and $\beta \approx 1$. The effect of intra-atomic orbital hybridization which modifies the atomic Hartree-Fock orbitals with respect to pure hydrogen-like $2p - 3p$ atomic orbitals, is estimated, from a full Hartree-Fock Si^+ atomic calculation, to further reduce Δ and the $2p_{z/x}$ exchange splittings by a factor of about 2, so that we arrive at the crude estimate $\Delta \approx 0.5eV$, $\epsilon_{2p_z\downarrow} - \epsilon_{2p_z\uparrow} \approx 1eV$, and $\epsilon_{2p_x\downarrow} - \epsilon_{2p_x\uparrow} \approx 0.1eV$. The overall picture for the Si-adatom $2p$ spectrum in absence of spin-orbit, but with all the previously described anisotropy effects included, is summarized in Fig. 1(b). When we include the spin-orbit interaction $\lambda_{\rm SO}\mathbf{L}\cdot\mathbf{S}$, the final core hole levels are obtained as in Fig. 2. For $\lambda_{\rm SO} = 0.4$ eV (the value extracted from the bulk $2p_{J=1/2} - 2p_{J=3/2}$ experimental core level splitting) we find a roughly three-peaked structure, the broad central peak four times as strong as each side peak. This offers an alternative explanation of the experimental lineshape [10] (see Fig. 2) in terms of a single exchange-split multiplet, rather than two chemically inequivalent sites S_1 and S_2 [10] whose existence is otherwise not supported. Incidentally, a similar three-peaked structure for the Si-2p core level spectrum has been experimentally observed for a sub-monolayer Si segregated at the surface of iron [11].

Additional direct experimental evidence for the Mott-Hubbard state could be obtained by a careful study of adatom ($3p_z$, $3p_z$) Auger spectral intensities, which should be easily singled out owing to the large gaps. The probability of double occupancy of the adatom dangling bond orbital should be almost completely suppressed, dropping from the band value of $1/4$, to a value of order t/U – where t is the hopping matrix element and U is the effective on-site Coulomb repulsion – which is one order of magnitude smaller. Even considering that only half of the orbital is adatom $3p_z$, this surface should show a ($3p_z$, $3p_z$) Auger intensity which, by comparison with the remaining $(3p, 3p)$ values, is anomalously small, as a proof of its Mott-Hubbard state.

Summarizing, we have argued that the Mott-Hubbard insulating surface state in SiC(0001) should leave clear and detectable intra-atomic fingerprints. The Si $2p$ core hole will exhibit a 6-fold multiplet resulting from the joint effect of intra-atomic exchange, asymmetry, and spin-orbit, with a characteristic three-peaked structure. Auger intensities should also be affected. More experimental and theoretical effort is clearly called for to check these strong correlations and related magnetic effects, possibly the first of this magnitude to be suggested for an sp-bonded, valence semiconductor surface.

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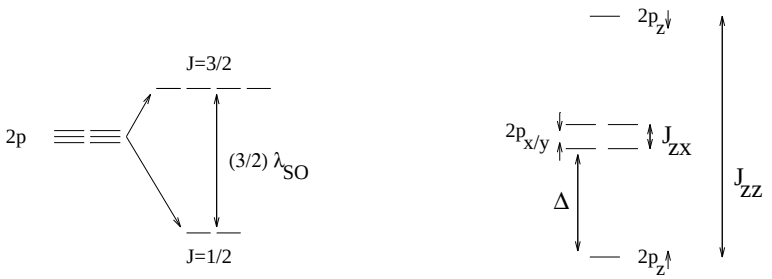
[11] G. Rossi, unpublished data. The possible connection between this experimental finding and our intra-atomic exchange picture needs to be further studied.

Figures



(a) (b)

FIG. 1. Schematic 2p core level energy scheme for a bulk Si atom (a), and for a spin-unpaired surface Si adatom (b). Estimates for the splittings in (b), discussed in the text, are $\Delta \approx 0.5$eV, $J_{zz} \approx 1$eV, and $J_{zx} \approx 0.1$eV.

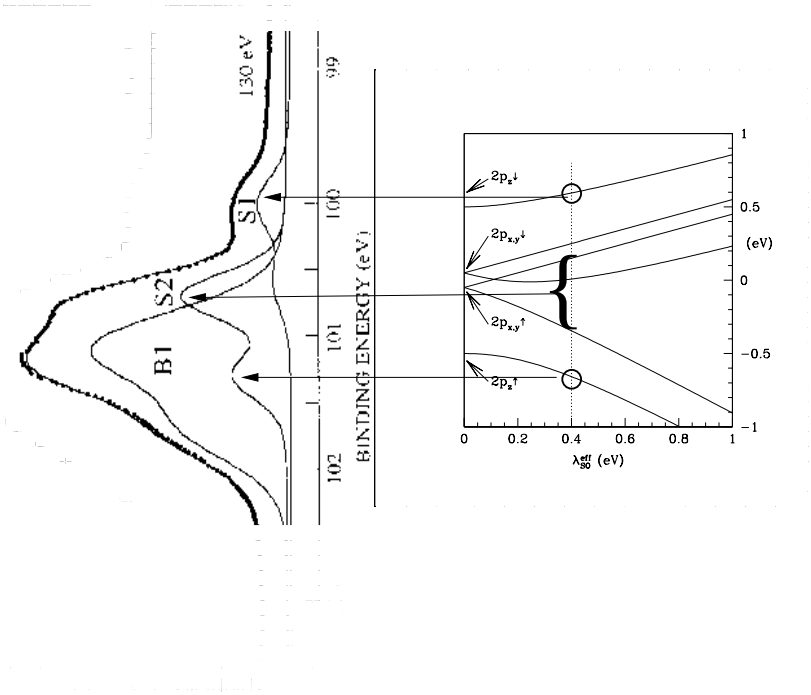


FIG. 2. Si 2p core levels calculated as a function of spin-orbit coupling, in comparison with photoemission data and original fitting in terms of bulk (B1) and two surface sites S1 and S2 by Johansson *et al.* [10]. Upon inclusion of intra-atomic exchange splitting the whole surface contribution S1+S2 can be explained as due to a single site. This figure is taken from Ref. [8].